

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C08K 3/22	A1	(11) International Publication Number: WO 99/37708 (43) International Publication Date: 29 July 1999 (29.07.99)
(21) International Application Number: PCT/US99/01050 (22) International Filing Date: 19 January 1999 (19.01.99) (30) Priority Data: 60/072,365 23 January 1998 (23.01.98) US 09/232,307 15 January 1999 (15.01.99) US (71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US). (72) Inventors: MAXWELL, Brian, Edison; 4 Shelldrake Court, Johnson City, TN 37601 (US). GIBSON, Philip, Edward; 2244 Charsley Road, Kingsport, TN 37660 (US). (74) Agent: HARDING, Karen, A.; P.O. Box 511, Kingsport, TN 37662-5075 (US).		(81) Designated States: BR, BY, CA, CN, JP, MX, RU, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: THERMOPLASTIC POLYMER COMPOSITION CONTAINING BLACK IRON OXIDE (57) Abstract Disclosed herein is a thermoplastic polymer composition comprising a blend of a thermoplastic polymer admixed with from about 5 to 50 ppm black iron oxide particles, based on the amount of said thermoplastic polymer. The black iron oxide is admixed with the polymer in order to speed up the process of reheating parisons formed from the polymer during bottle manufacturing. The composition has the beneficial combination of a large percent reheat rate improvement (RIV) with only a small decrease in transparency (ΔL^*). The ratio of RIV/ ΔL^* is significantly better than carbon black-polymer blends having similar RIV.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	IS	Iceland	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

THERMOPLASTIC POLYMER COMPOSITION CONTAINING BLACK IRON OXIDE

5 This patent application claims the benefit of U.S. Provisional Patent Application, serial number 60/072,365, filed January 23, 1998.

FIELD OF THE INVENTION

10 The present invention relates to the production of clear, colorless thermoplastic polymer having improved reheat. The present invention is particularly useful in the field of beverage bottle manufacturing.

BACKGROUND

15 Heat lamps used for reheating polymer preforms (parisons) for the commercial manufacture of beverage bottles are typically quartz lamps having a broad light emission spectrum from 500 nm to greater than 1500 nm. The maximum light emission from quartz lamps occurs in the range of about 1100-1200 nm. Polyester, especially polyethylene terephthalate ("PET"), absorbs poorly in the region between 500 and 1400 nm. So in order to speed up the reheat step in bottle production, agents which absorb light in the 700-1200 nm range can be added to the polyester polymer.

20 A variety of black and gray body absorbing compounds have previously been used as reheat agents to improve the heat up characteristics of polyester under quartz lamps. However, these compounds impart color to polymers. Therefore, the amount of absorbing compounds that can be added to a polymer is limited by its impact on the visual properties of the polymer, such as transparency. Transparency is represented as "L*" in the Gardner Color System, with an L* of 100 representing 100% transparency and an L* of 0 representing 100% opacity. Generally, darker colored reheat agents can be added in only very small quantities because of their negative impact on L*.

25

30

Previously disclosed examples of useful polymer reheat agents include carbon black (US 4,408,004) and reduced antimony metal (US 5,419,936 and US 5,529,744). Additionally, US 4,420,581 and US 4,250,078 disclose using red iron oxide as an infrared absorber in polyester containing green dye. The red tint
5 added by the red iron oxide is not problematic in that use because the green dye masks the red tint. While colorless and green beverage bottles have been found to be commercially useful, red tinted bottles have not been marketable. Without the masking presence of a green dye, red iron oxide would cause an undesirable red hue to an otherwise colorless, or neutral hue, polyester bottle.

10 A more darkly colored absorbing compound generally improves heat up characteristics better than a relatively lighter absorbing compound. However, the more darkly colored absorbing compounds can only be added in very small quantities due to the larger negative impact on L^* . For example, when carbon black, a very dark black compound, is added to PET in concentrations greater
15 than a few ppm, bottles blown from that PET are very gray and dull in appearance. Reduced antimony metal can be present in PET in concentrations up to about 50 ppm without having an excessive negative impact on L^* because reduced antimony is a gray metal which is much lighter in color than true black body absorbers like carbon black.

20 U.S. Patent 4,481,314, discloses the use of certain anthraquinone type dyes for the purposes of improving reheat rates. However, these dyes have substantial absorbance in the visible spectrum, resulting in coloration of the polymer. In addition, their relatively low molar extinction coefficients (ϵ) (in the range of 20,000) require the use of relatively large amounts of the dye (20-100
25 ppm) to the polymer. At a concentration of 50 ppm, the reheat rate improvement was 7%. However, at these levels the polymer displays a light green color which is not suitable for producing clear, neutral hue bottles.

In light of the above, it would be desirable to have an infrared absorber material which can be added to a thermoplastic polymer in a concentration
30 sufficient to effectively increase the reheat rate of the polymer by about 10

percent, yet without deleteriously affecting polymer L* as much as previously known effective polymer reheat agents.

SUMMARY OF THE INVENTION

5 The present invention is a thermoplastic polymer composition which comprises a blend of a thermoplastic polymer admixed with from about 5 to 50 ppm black iron oxide particles, based on the amount of said thermoplastic polymer.

10 DETAILED DESCRIPTION OF THE INVENTION

 The applicants have found that black iron oxide (Fe_3O_4) is a very effective polyester reheat agent when used in a relatively high concentration of up to about 50 ppm. The increase in polymer reheat rate using 50 ppm of black iron oxide is comparable to the increase in polymer reheat rate provided by the
15 addition of merely about 5 ppm black iron oxide. It was found that, despite the fact that a much higher concentration of a black iron oxide must be admixed in a polymer to attain the same increase in reheat rate, the increase in reheat rate is achieved with comparatively less detrimental affect on polymer L* using black iron oxide.

20 A further benefit of the present invention is that, unlike other black or gray body absorbing compounds, black iron oxide is readily and quantitatively measurable in the resultant polyester composition due to the detectability of iron. This provides a significant improvement in processing and production control over the amount of absorbing agent admixed with the polymer since carbon black
25 and antimony metal cannot be quantitatively distinguished from the other forms of carbon and antimony which are inherently present in polyester.

 The present invention is a thermoplastic polymer composition which comprises a blend of a thermoplastic polymer admixed with from about 5 to 50 ppm black iron oxide (Fe_3O_4), based on the amount of polymer. An article such
30 as a beverage bottle formed from the present composition will display an L* just

slightly lower (less transparent) than the L^* of an article formed from the same polymer without the presence of black iron oxide. The present polymer composition has an improved (less) reheat time under a quartz lamp of up to about 15 percent.

5 The thermoplastic polymer composition of the present invention has an unexpectedly high ratio of reheat rate improvement to transparency change ($RIV/\Delta L^*$), when compared to a composition that is the same except for an absence of iron oxide. The percent reheat improvement (RIV) is the improvement in polymer reheat rate after admixing black iron oxide to the polymer. ΔL^* is the amount of change in the transparency of the polymer upon admixing the black iron oxide with the polymer. The ratio of RIV to ΔL^* for the composition of the present invention is preferably greater than about 2.0, more preferably greater than about 2.5. For comparison, the ratio of RIV to ΔL^* for thermoplastic polymer admixed with carbon black is about 1.5. Hence, the ratio of RIV to ΔL^* of the composition of the present invention is superior to that of carbon black polymer compositions having similar RIV.

15 The composition of the present invention is preferably made by admixing black iron oxide particles to the polymer reactant system, during or after polymerization, to the polymer melt, or to the molding powder or pellets from which the bottle parisons are formed. In order to achieve adequate mixing, the black iron oxide should be added to a polymer while at an inherent viscosity (I.V.) of about 0.6 to 0.8 dL/g, measured at 25°C in a 60/40 wt/wt phenol/tetrachloroethane.

25 The suitable concentration of black iron oxide in the present polymer composition is between about 5 to 50 ppm, preferably between about 7 to 30 ppm, with a concentration of about 10 to 20 ppm being more preferred. The concentration of black iron oxide is based on the amount of polymer in the composition.

30 The average particle size of the black iron oxide used in the present invention is preferably between about 0.1 to 10 μm (micrometers), more

preferably between about 0.5 to 5 μm . The presence of larger particles would cause a bottle formed from the polymer composition to become hazy.

The thermoplastic polymers in the present composition can be any crystallizable thermoplastic homopolymer or copolymer. However, the thermoplastic polymer used in the present invention is most usefully a polyester, particularly a partially aromatic polyester, especially a polyester derived, at least mainly, from an aromatic diacid and an aliphatic diol. The preferred polyester is one which comprises at least 70 mole percent, and more preferably at least 85 mole percent, of units of ethylene terephthalate.

In addition to units derived from terephthalic acid, the acid component of the present polyester may be modified with units derived from one or more additional dicarboxylic acids. Such additional dicarboxylic acids include aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms, or cycloaliphatic dicarboxylic acids preferably having 8 to 12 carbon atoms. Examples of dicarboxylic acid units useful for modifying the acid component are units from phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, and the like, with isophthalic acid, naphthalene-2,6-dicarboxylic acid, and cyclohexanedicarboxylic acid being most preferable. It should be understood that use of the corresponding acid anhydrides, esters, and acid chlorides of these acids is included in the term "dicarboxylic acid".

In addition to units derived from ethylene glycol, the diol component of the present polyester may be modified with units from additional diols including cycloaliphatic diols preferably having 6 to 20 carbon atoms and aliphatic diols preferably having 3 to 20 carbon atoms. Examples of such diols include diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-

ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, and 2,2-bis-(4-hydroxypropoxyphenyl)-propane.

5 Polymers of the present invention can be prepared by conventional polymerization procedures well-known in the art. Polyester polycondensation processes include direct condensation of dicarboxylic acid with the diol, ester interchange, and solid state polymerization methods. Typical polyesterification catalysts which may be used include titanium alkoxides, dibutyl
10 tin dilaurate, and antimony oxide or antimony triacetate, used separately or in combination, optionally with zinc, manganese, or magnesium acetates or benzoates and/or other such catalyst materials as are well known to those skilled in the art. Phosphorus and cobalt compounds may also optionally be present.

Other components can be added to the composition of the present
15 invention to enhance the performance properties of the polyester composition. For example, crystallization aids, impact modifiers, surface lubricants, denesting agents, stabilizers, antioxidants, ultraviolet light absorbing agents, metal deactivators, colorants, nucleating agents, acetaldehyde reducing compounds, other reheat reducing aids, fillers and the like can be included. The resin may
20 also contain small amounts of branching agents such as trifunctional or tetrafunctional comonomers such as trimellitic anhydride, trimethylolpropane, pyromellitic dianhydride, pentaerythritol, and other polyester forming polyacids or polyols generally known in the art. All of these additives and many others and their use are well known in the art and do not require extensive discussion. Any
25 of these compounds can be used in the present composition as long as they do not hinder the present invention from accomplishing its objectives. Therefore, it is preferable that the present composition be essentially comprised of a blend of thermoplastic polymer and black iron oxide, with only a modifying amount of other ingredients being present.

The polymer composition of the present invention may be used to form bottle parisons, also known as preforms, which are test tube shaped, injection molded articles. A parison is typically heated to about 10°C above the glass transition temperature of the polymer composition by passing the parison in front of a bank of quartz infrared heating lamps, positioning the parison in a bottle mold, and then blowing pressurized air through the open end of the mold.

The present invention is illustrated by the examples below. However, the examples should not be interpreted as a limitation on the present invention.

10 EXAMPLES

Polyethylene terephthalate (PET) polymer compositions were made containing varying levels of black iron oxide (BIO) and carbon black (CB). The relative reheat rates of the polymers were measured as follows:

The polymer samples were injection molded into 3" x 3" x 0.150" flat plaques. The plaques were set aside for 24 hours to come to ambient temperature. A set of four reference standard plaques and four plaques of each sample material were treated as follows.

A plaque was placed in a wooden holder that only contacted the plaque on the edges. The temperature of the plaque in the holder was measured. This was the initial temperature (T_i). The holder was moved into position a fixed distance in front of a tungsten quartz heat lamp identical to those used in reheat blow molding machines. The lamp was tuned to emit light at a temperature of 4,000 degrees Fahrenheit (λ_{max} approximately 1,100 nm). The lamp was turned on for 35 seconds. Then the temperature of the plaque was read by an infrared pyrometer. The temperature was read from the face of the plaque which was not illuminated. This was done to allow the heat absorbed by the front surface of the plaque to soak through the plaque. The temperature of the back side of the plaque rises at first to a maximum temperature and then begins to fall slowly as the entire plaque cools. The maximum temperature was recorded as the final temperature (T_f).

The temperature rise was recorded as ΔT ($T_f - T_i$). The change in temperature was also adjusted for small differences in the thickness of the plaques. The adjusted ΔT was then averaged over the four plaques to give the ΔT_{avg} for each sample. The ΔT_{avg} for each sample was divided by the ΔT of the concurrently tested reference standard to provide the Reheat Index Value (RIV) = $(\Delta T_{avg} \text{ Sample} \div \Delta T_{avg} \text{ Reference})$.

Percent Reheat Improvement was calculated as

$$\% \text{ Reheat Improvement} = ((RIV_{\text{sample}} - RIV_{\text{control}}) \div RIV_{\text{control}}) \times 100$$

10

Table 1 below shows that, at equivalent improvements in reheat (RIV), the black iron oxide (BIO) samples displayed better L^* , compared to the carbon black (CB) samples. This property is quantified below as $RIV / \Delta L^*$.

15

Table 1

Additive	Conc. (ppm)	RIV	L^*	ΔL^*	$RIV / \Delta L^*$
BIO Control	0	0.00%	86.30		
BIO Control	0	0.00%	85.81	0.00	
BIO	2	0.29%	85.78	-0.03	9.67
BIO	5	3.17%	84.54	-1.27	2.50
BIO	8	6.35%	83.09	-2.72	2.33
CB Control	0	0.00%	86.60		
CB Control	0	0.00%	86.44	0.00	
CB	0.5	2.85%	84.07	-2.37	1.20
CB	1	5.72%	82.18	-4.26	1.34
CB	2	10.07%	79.56	-6.88	1.46
CB	4	19.40%	73.37	-13.07	1.48
Sb Metal	?		83.44		

The results from Table 1 were plotted as a function of reheat additive concentration to predict performance at higher and lower concentrations to determine that the black iron oxide concentration limits of the composition of the present invention are between about 5 to 50 ppm.

CLAIMS

We Claim:

1. A thermoplastic polymer composition comprising a blend of a thermoplastic polymer admixed with from about 5 to 50 ppm black iron oxide particles, based on the amount of said thermoplastic polymer.
2. The composition of Claim 1 having a ratio of percent reheat rate improvement to transparency change ($RIV/\Delta L^*$) greater than about 2.0, wherein the RIV and ΔL^* are determined based on a composition that is the same except for an absence of iron oxide.
3. The composition of Claim 1 wherein the concentration of black iron oxide is about 7 to 30 ppm.
4. The composition of Claim 1 further wherein said particles have a particle size of about 0.1 to 10 μm .
5. The composition of Claim 1 wherein said thermoplastic polymer is a polyester.
6. The composition of Claim 5 wherein said polyester comprises between about 70 to 100 mole percent repeat units from ethylene terephthalate.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/01050

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K3/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 191 240 A (MITSUI PETROCHEMICAL IND) 20 August 1986 see page 3, line 11 - line 12 see claim 1	1,3
Y	US 4 250 078 A (MCFARLANE FINLEY E ET AL) 10 February 1981 cited in the application see the whole document	1-6
Y	GB 2 165 547 A (GINEGAR KIBBUTZ) 16 April 1986 see claims 1-4	1-6

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

*** Special categories of cited documents :**

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

10 May 1999

Date of mailing of the international search report

18/05/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Siemens, T

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/01050

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0191240 A	20-08-1986	AU 582407 B	23-03-1989
		AU 5139485 A	26-06-1986
		CA 1286830 A	23-07-1991
		DE 3587289 A	27-05-1993
		DE 3587289 T	28-10-1993
		JP 2002577 C	20-12-1995
		JP 7035452 B	19-04-1995
		JP 61268744 A	28-11-1986
		US 4731400 A	15-03-1988
US 4250078 A	10-02-1981	US 4420581 A	13-12-1983
GB 2165547 A	16-04-1986	DE 3531878 A	13-03-1986
		FR 2569707 A	07-03-1986
		JP 61111341 A	29-05-1986
		NL 8502431 A	01-04-1986
		US 4895904 A	23-01-1990



7